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PATENT

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Cesur CELIK et al.

Serial No.: 10/826,681

Filed: April 16, 2004

Title: LAMINATED CERAMIC CAPACITOR

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PATENT



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Applicant: Cesur CELIK et al

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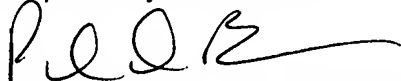
S I R :

Enclosed is a certified copy of the corresponding Canadian patent application for which priority is claimed under 35 USC 119.

<u>Country</u>	<u>Application No.</u>	<u>Filing Date:</u>
CANADA	CA2359347	October 18, 2001

No fee is believed to be due with this submission. However, if any fees are due, please charge any required fee (or credit any overpayments of fees) to the Deposit Account of the undersigned, Account No. 500601 (Docket No. 7012-X04-002).

Respectfully submitted,


Paul D. Bianco, Reg. #43,500

Enclosures

Paul D. Bianco
FLEIT KAIN GIBBONS GUTMAN BONGINI & BIANCO
21355 E. Dixie Highway, Suite 115
Miami, Florida 33180
Tel: 305-830-2600; Fax: 305-830-2605
E-mail: PBianco@@FocusOnIP.com



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Specification and Drawings, as originally filed, with Application for Patent Serial No:
CA 2359347 on October 18, 2001, by **CANADIAN ELECTRONIC POWDERS
CORPORATION (CEPC)**, assignee of Serge Grenier and Cesur Celik, for "Laminated
Ceramic Capacitor Internal Electrode Material".

Bracy Paulhus
Agent certificateur/Certifying Officer
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ABSTRACT

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The present invention provides a laminated ceramic capacitor with an internal electrode comprising a sintered alloy containing at least two alloying elements selected from the group consisting of Ni, Cu, Cr, Sn, Mn, Co and/or

10 W.

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LAMINATED CERAMIC CAPACITOR INTERNAL ELECTRODE MATERIAL

BACKGROUND OF THE INVENTION

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The present invention relates to laminated ceramic capacitors also known as multi layered ceramic chip capacitors (MLCC), particularly to internal electrode material for such capacitors.

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Multi layered ceramic chip capacitors generally consist of a dielectric ceramic matrix with embedded metal sheet electrodes of some μm thickness and some 10 μm of distance. In manufacturing such capacitors, suitable pastes of powdered ceramic matrix precursor material and suitable pastes of a metal powder are alternatively laminated on each other. Sometimes there is also provided a thin intermediate material.

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After lamination the laminate is dried and heated to about 300 to 450°C (normally under air) to decompose the organic binder of the pastes. Thereafter the laminate is further heated under vacuum or inert gas atmosphere to about 1200 to 1350°C for sintering and formation of the ceramic dielectric material.

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During the decomposition step there is a risk that the metallic powder of the internal electrode material is oxidized, which will be deoxidized during heating to the sintering temperature. Deoxidation during sintering leads to shrinkage of the internal electrode causing cracks and delamination of the capacitor and high percentages of rejections from the manufacturing process.

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Most of the multilayered ceramic chip capacitors use Pd or Pd alloys as the internal electrode material, which is sufficient resistant to oxidation, whereby deoxidation shrinkage is avoided.

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Recent developments try to replace the precious Pd metal with Base Metal Electrode (BME) materials such as Ni or Cu with small alloying additives such as Mg, Ca (US

patent 6,162,277 to Toshima et al.) or 95 % Ni having at least one alloying additive of Mn, Cr, Co, Al or P (US patent 5,319,517 to Nomura et al.).

SUMMARY OF THE INVENTION

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An object of the present invention is to provide a particulate Base Metal Electrode material useful for internal electrodes of laminated ceramic capacitors providing for an improved resistance to oxidation.

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Another object of the present invention is to provide Base Metal powders, which after sintering in an MLCC capacitor provide good or at least acceptable electronic conductivity.

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Another object of the present invention is to provide for a multilayer ceramic chip capacitor being less prone to cracking.

Another object of the invention is to reduce the number of rejections of MLCC capacitors having Base Metal electrodes.

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The present invention concerns base metal alloy powders, having a mean particle size of below 1 μm , comprising binary or ternary alloys of Ni, Cu, Cr and/or Sn and optionally containing minor amounts of additional alloying elements.

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In general, fine metal and alloy powders are characterized by a large surface area. Since the oxidation reaction takes place on the exterior surface of the individual particles, the greater the surface area of the powder, the more prone it is to oxidize. Oxidation reactions are exothermic (i.e. they generate heat). Because of their very high surface areas, fine powders tend to readily react with oxygen. This rapid oxidation results in a sudden local high temperature rise, which in turn can lead to undesirable changes in sinterability and delamination of the MLCC. Depending upon the selection of alloying elements, in alloy powders, interdiffusion of the alloying elements

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will depend on their respective affinity to oxygen and the permeability of the oxide layer formed. If the interdiffusion velocity of the alloying elements is larger than the diffusion velocity of oxygen in the alloy, the metal of higher oxygen affinity may diffuse to the surface and fix oxygen at the surface, which leads to increased oxidation resistance of the powder. Maximum oxidation stability may occur at certain alloying ratio of the alloying elements and may not be achieved at complete segregation of the alloying elements. The situation is more complicated in the case of more than two alloying elements due to the relative influence of the alloying partners to each other as regards diffusivity and oxygen affinity.

According to the broad concept presented, the present invention comprises alloy powders containing at least two alloying elements selected from the group of Ni, Cu, Cr, Sn, Mn, Co and W comprising

- 1 to 99 weight-% of nickel,
- 1 to 99 weight-% of copper,
- 6 to 60 weight-% of chromium,
- 6 to 15 weight-% of tin,
- 6 to 15 weight-% of manganese,
- 6 to 15 weight-% of cobalt, and/or
- 6 to 15 weight-% of tungsten.

Said alloy may additionally contain at least one of the elements (other than the at least two alloying elements mentioned above) selected from Ag, Al, Au, B, Be, Ca, Ce, Co, Cr, Cu, Fe, Ge, Hf, Mg, La, Nb, Ni, Mn, Mo, Si, Sn, P, Pd, Pt, Ta, Ti, V, W, Y, Zn and Zr in an amount of about 0,1 to 20 weight-% based on total metal. The additional alloying elements may be present in an amount of 0,1 to 20 wt% based on the total metal. Preferably at least two of the additional alloying elements are present in the alloy powder. The total amount of additional alloying elements in the alloy powder is preferably less than 6 wt% based on the total metal.

Preferred binary alloy powders comprise

nickel-copper alloys having 1-99 wt% of nickel, more preferably 6-94 wt% of nickel, particularly preferred 6-40 wt% of nickel or 6-40 wt% of copper and most preferred 15-30 wt% of Ni; nickel-chromium alloys having 6-60wt% of chromium, more preferably less than 40 wt% of chromium; copper-tin alloys containing 2 to 15 wt% of tin, more preferably 3-12 wt% of tin, and particularly preferred more than 6 wt% of tin.

The preferred binary alloys may become ternary or quaternary alloys by including one or two of the additional alloying elements.

Preferred ternary alloy powders comprise copper-nickel-chromium alloys containing 50-94 wt% Cu, 0,2-40 wt% Ni, and 0,2-30 wt% Cr, preferably 60-90 wt% Cu, 2-25 wt% Ni, and 0,5-20 wt% Cr; copper-nickel-tin alloys containing 60-95 wt% Cu, 1-30 wt% Ni and 0,2 to 10 wt% tin, preferably 60-80 wt% Cu, 10-25 wt% Ni and 2-10 wt% tin.

The preferred ternary alloys may become quaternary alloys by including one of the additional alloying elements.

The powders according to the invention preferably have a particle size as derived from measurement of the specific surface area according to the BET method of 100 to 700 nm, preferably below 600 nm, more preferably from 100 to 500 nm. For practical reasons resulting from manufacturing methods of MLCC capacitors, presently particles sizes of 250-400 nm are of particular use, however improved such methods which are already experimentally in use will allow to use powders in the lower range of 100 to 300 nm. Preferably the powders of the invention have substantially spherical shape.

The powders may be manufactured according to any known method of manufacture of fine particle powders, such as gel precipitation method with subsequent reduction of the precipitate, CVR methods by evaporation of suitable metal compounds such as

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chlorides in hydrogen containing gas atmosphere and condensation of metal powder, evaporation of metals in a plasma arc and controlled condensation of gaseous metals. The preferred method according to the invention is a transferred arc plasma method as disclosed in WO 00/10756, the disclosure of which is included herein by reference.

Although most of these methods are disclosed for the manufacture of pure metal powders only, there is no principal difficulty to modify these methods to allow the manufacture of alloys of defined composition. Coprecipitation in the gel precipitation process is well known. In CVR methods either mixtures of the precursor compounds may be evaporated from a single source or separate evaporators may be used and the reactant gases may be introduced into the reaction and condensation tube via separate inlets into the tube.

In the preferred transferred arc plasma method evaporation occurs from a melt of the metal hit by the plasma arc. The melt must have a composition different from the composition of the desired alloy powder to compensate for different evaporation rates of the alloying elements. Preferred is the continuous production method also disclosed in WO 00/10756, wherein the alloying elements are continuously fed into the crucible of the plasma chamber at the desired alloying ratio, preferably in the form of prealloyed material. After some time of production composition of the melt will vary to assume a composition from which the desired composition evaporates. If the required melt composition is known, the crucible may be filled at the start of production with a composition from which the desired alloy composition evaporates. The required melt composition can roughly be estimated from known vapor pressure versus temperature relations of the alloying elements. Principally, it is also possible to have two or more plasma chambers from which the alloying elements are separately evaporated with introduction of the gases into a common condensation and cooling tube.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are intended to disclose the invention in more detail without limiting the generality of the disclosure hereof.

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An experimental set up as disclosed in WO 00/10756 has been used. Prealloyed materials are filled into the crucible of the transferred arc system. The alloying ratio of the prealloyed precursor powder was roughly selected at a modified ratio of the desired alloying ratio taking into account different evaporation velocities of the elements from the molten alloy. Argon was used as the plasma torch gas, the diluting gas and the cooling gas.

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Samples of the formed alloy powder were taken at different times during one experiment. Due to the non-optimized precursor composition for a specific desired alloying ratio, differently composed alloy powders have been obtained during each single experiment. Table 1 shows the composition of the starting melts during the various runs.

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Table 1:

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Run	Compositon of starting melts in wt%
A	85 Cu + 15 Sn
B	30 Cu + 69 Ni + 1 (Al+Si)
C	50 Cu + 50 Ni
D	42 Cu + 58 Ni
E	95.1 Ni + 4.1 Cr + 0.8 Cu
F	87.9 Ni + 11.9 Cr + 0.2 Cu
G	73.6 Ni + 26 Cr + 0.4 Cu
H	99 Cu + 1 Mn
J	91 Ni + 9 Co
K	40 Ni + 60 W

The various powders obtained were analysed for chemical composition, particle size derived from BET specific surface area measurement, and the onset of oxidation as

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determined by DTA-analysis. The results are shown in the following tables 2, 3 and 4.

5 Fig. 1 exemplifies a DTA curve also comparing the second pure Cu sample with sample B6.

Samples of the powder were subjected to x-ray diffraction analysis, using $\text{CuK}\alpha$ radiation. Fig. 2 shows such typical spectrum for sample E2, indicating excellent crystallinity of the powder.

Table 2:

Powder	Composition (wt%)							Size	Onset of oxidation
run/ sample	Cu wt%	Sn wt%	Ni wt%	Al ppm	Si 2) ppm	O ppm	C ppm	nm	°C
pure Cu	100	--	--	--	--	5500	150	407	180
	100	--	--	--	--	5500	150	541	190
A1	89.3	10.7	<0.01	<9	200	6100	600	534	1)
B1	82.2	--	15.2	560	1040	8135	687	193	161
B2	76.8	--	22	680	2150	4984	162	346	168
B3	73.5	--	25.1	730	2250	5420	180	424	366
B4	70.2	--	28.3	780	2350	5850	197	415	398
B5	68.7	--	29.7	755	1800	7080	230	343	371
B6	67.3	--	31.1	730	1250	8300	267	273	370
C1	81.2	--	18.5	4	1700	7220	200	339	327
D1	84.4	--	14.8	1	1100	5620	200	489	331
D2	83.1	--	16.5	6	1100	??	??	482	343
D3	80.3	--	18.6	2	200	8490	200	458	344
D4	80.8	--	18.8	8	1000	6840	200	545	357
D5	77.3	--	22.3	9	1400	??	??	541	359

- 1) small DTA-response at 160°C; no main onset of oxidation below 550°C
- 2) unknown content in precursor material

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Table 3:

powder	Composition				Size	Onset of oxidation
run/ sample	Ni wt%	Cr wt%	Cu wt%	O ppm	nm	°C
pure Ni	100	--	--	2500	300	360-380
	100	--	--	to	400	380-400
	100	--	--	5000	500	400-420
	100	--	--		600	450-500
E1	90.2	6.1	3.7	??	396	531
E2	88.4	6.3	4.6	4710	464	534
E3	90.3	6.7	2.4	4920	462	522
F1	86.9	10.9	0.6	??	436	528
F2	88	11	0.5	??	626	551
G1	63.6	35.7	0.35	8780	606	>580
G2	61.5	37.3	0.8	9130	508	565
G3	58.4	39.4	1.66	12120	295	568

Table 4:

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Powder	Composition						Size	Onset of Oxidation
run/ sample	Ni wt%	Cu wt%	Mn wt%	Co wt%	W wt%	O ppm	nm	°C
H1	--	88.7	10.9	--	--	7840	486	388
J1	87.8	--	--	11.2	--	5180	510	568
K1	89.7	--	--	--	9.6	6330	473	487

Claims:

1. A laminated ceramic capacitor with an internal electrode wherein said electrode comprises a sintered alloy containing at least two alloying elements selected from the group of Ni, Cu, Cr, Sn, Mn, Co and W comprising
 - 1-99 weight-% Ni,
 - 1-99 weight-% Cu,
 - 6-60 weight-% Cr,
 - 6-15 weight-% Sn,
 - 6-15 weight-% Mn,
 - 6-15 weight-% Co, and/or
 - 6-15 weight-% W
2. A capacitor according to claim 1, wherein said alloy additionally contains at least one of the elements selected from Ag, Al, Au, B, Be, Ca, Ce, Co, Cr, Cu, Fe, Ge, Hf, Mg, La, Nb, Ni, Mn, Mo, Si, Sn, P, Pd, Pt, Ta, Ti, V, W, Y, Zn and Zr in an amount of about 0,1 to 20 weight-% based on total metal.
3. A capacitor according to claim 2, wherein said alloy contains at least two of the said additional elements.
4. A capacitor according to claim 2, wherein the said additional elements are present in said alloy in an amount of up to 6 weight-%.
5. A capacitor according to one of claims 1 to 4, wherein said alloy is a nickel-chromium alloy containing from about 6 to about 40 weight-% of chromium.
6. A capacitor according to one of claims 1 to 4, wherein said alloy is a nickel-copper-chromium alloy containing from about 0,2 to 30 weight-% of copper.

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7. A capacitor according to one of claims 1 to 4, wherein said alloy is nickel-copper-chromium alloy containing from about 0,2 to 30 weight-% of chromium.
- 5 8. A capacitor according to one of claims 1 to 4, wherein said alloy is a copper-nickel-chromium alloy containing from about 0,2 to 30 weight-% of nickel.
9. A capacitor according to one of claims 1 to 4, wherein said alloy is a copper-nickel-chromium alloy containing from about 0,2 to 30 weight-% of chromium.
10
10. A capacitor according to one of claims 1 to 4, wherein the said alloy is a copper-tin-nickel alloy containing 1 to 30 weight-% of nickel.
- 15 11. A capacitor according to one of claims 1 to 4 and 8 to 10, wherein said alloy contains at least 60 weight-% of copper.
12. A capacitor according to one of claims 1 to 6, wherein said alloy contains at least 60 weight-% of nickel.
20
13. A capacitor according to one of claims 1 to 12, wherein the powder has an average particle size of about 100 to 700 nm as derived from BET-measurement.
- 25 14. A capacitor according to one of claims 1 to 13, wherein the powder has substantially spherical shape.
15. A base metal alloy powder containing at least two alloying elements selected from the group of Ni, Cu, Cr, Sn, Mn, Co and W comprising
30 1-99 weight-% Ni,
1-99 weight-% Cu,

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- 5 6-60 weight-% Cr,
 6-15 weight-% Sn,
 6-15 weight-% Mn
 6-15 weight-% Co and/or
 6-15 weight-% W.
- 10 16. A base metal alloy powder according to claim 15, wherein said alloy additionally contains at least one of the elements selected from Ag, Al, Au, B, Be, Ca, Ce, Co, Cr, Cu, Fe, Ge, Hf, Mg, La, Nb, Ni, Mn, Mo, Si, Sn, P, Pd, Pt, Ta, Ti, V, W, Y, Zn and Zr in an amount of about 0,1 to 20 weight-% based on total metal.
- 15 17. A base metal alloy powder according to claim 16, wherein said alloy contains at least two of the said additional elements.
18. A base metal alloy powder according to claim 16, wherein the said additional elements are present in said alloy in an amount of up to 6 weight-%.
- 20 19. A base metal alloy powder according to one of claims 15 to 18, wherein said alloy is a nickel-chromium alloy containing from about 6 to about 40 weight-% of chromium.
- 25 20. A base metal alloy powder according to one of claims 15 to 18, wherein said alloy is a nickel-copper-chromium alloy containing from about 0,2 to 30 weight-% of copper.
- 30 21. A base metal alloy powder according to one of claims 15 to 18, wherein said alloy is a copper-nickel-chromium alloy containing from about 0,2 to about 30 weight-% of nickel.

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22. A base metal alloy powder according to one of claims 15 to 18, wherein said alloy is a copper-nickel-chromium alloy containing from about 0,2 to about 30 weight-% of chromium.
- 5 23. A base metal alloy powder according to one of claims 15 to 18, wherein said alloy is nickel-copper-chromium alloy containing from about 0,2 to 30 weight-% of chromium.
- 10 24. A base metal alloy powder according to one of claims 15 to 18, wherein the said alloy is a copper-tin-nickel alloy containing 1 to 30 weight-% of nickel.
25. A base metal alloy powder according to one of claims 15 to 18 and 22 to 24, wherein said alloy contains at least 60 weight-% of copper.
- 15 26. A base metal alloy powder according to one of claims 15 to 20, wherein said alloy contains at least 60 weight-% of nickel.
- 20 27. A base metal alloy powder according to one of claims 15 to 26, wherein the powder has an average particle size of about 100 to 700 nm as derived from BET-measurement.
28. A base metal alloy powder according to one of claims 15 to 27, wherein the powder has substantially spherical shape.

Fetherstonhaugh & Co.
Ottawa, Canada
Patent Agents

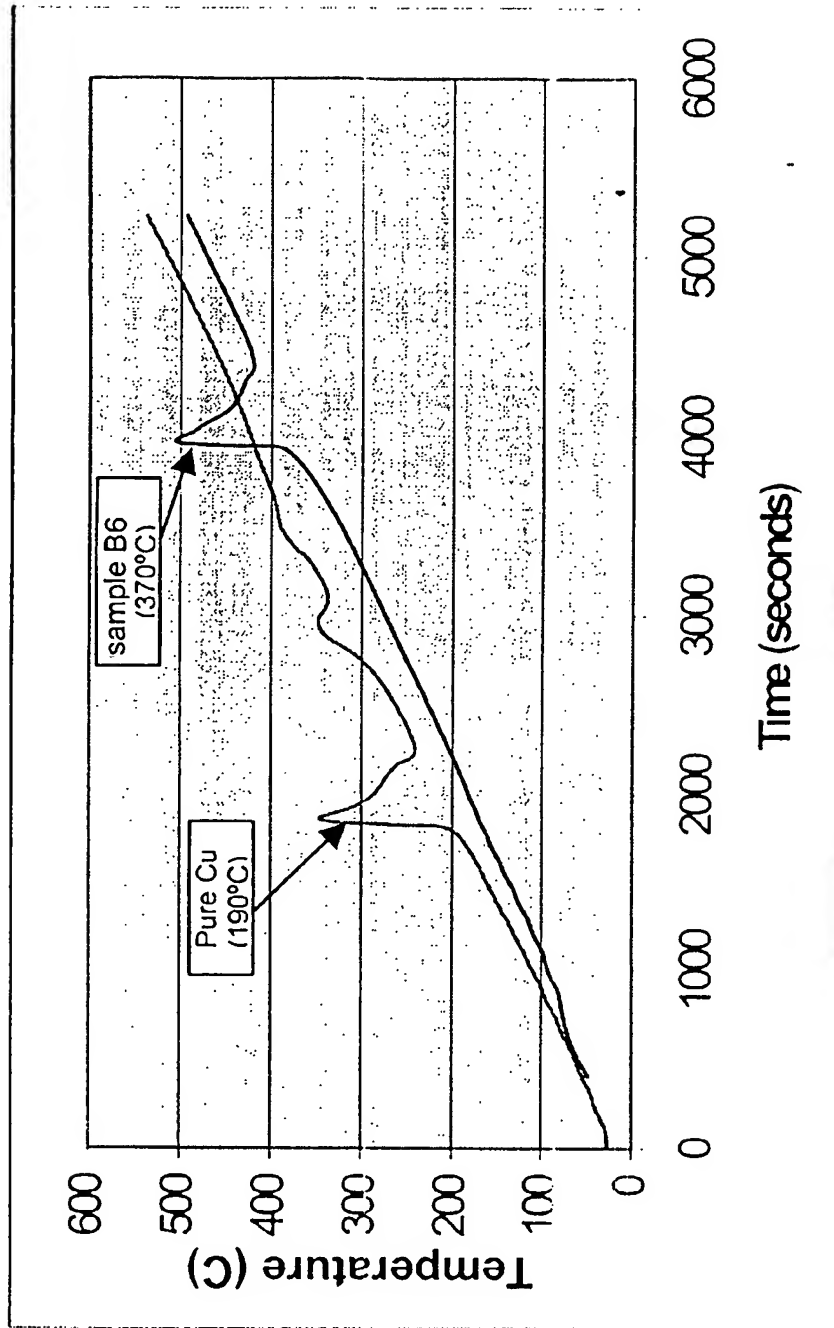


Fig. 1

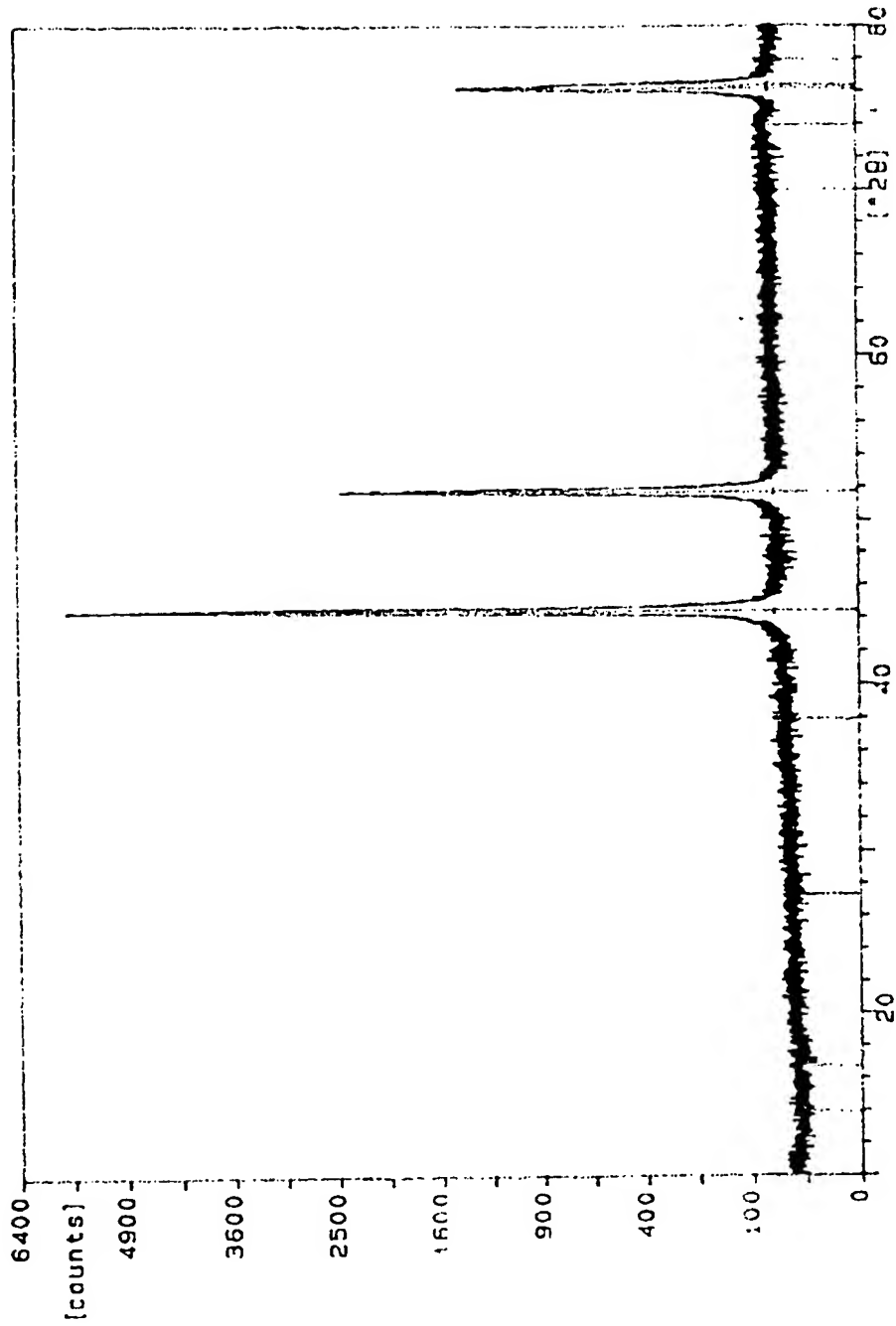


Fig. 2